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Biodiesel production from *Jatropha curcas* oil

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ABSTRACT

In view of the fast depletion of fossil fuel, the search for alternative fuels has become inevitable, looking at huge demand of diesel for transportation sector, captive power generation and agricultural sector, the biodiesel is being viewed a substitute of diesel. The vegetable oils, fats, grease are the source of feedstocks for the production of biodiesel. Significant work has been reported on the kinetics of transesterification of edible vegetable oils but little work is reported on non-edible oils. Out of various non-edible oil resources, *Jatropha curcas* oil (JCO) is considered as future feedstocks for biodiesel production in India and limited work is reported on the kinetics of transesterification of high FFA containing oil. The present study reports a review of kinetics of biodiesel production. The paper also reveals the results of kinetics study of two-step acid–base catalyzed transesterification process carried out at pre-determined optimum temperature of 65 and 50 °C for esterification and transesterification process, respectively, under the optimum condition of methanol to oil ratio of 3:7 (v/v), catalyst concentration 1% (w/w) for H_2SO_4 and NaOH and 400 rpm of stirring. The yield of methyl ester (ME) has been used to study the effect of different parameters. The maximum yield of 21.2% of ME during esterification and 90.1% from transesterification of pretreated JCO has been obtained. This is the first study of its kind dealing with simplified kinetics of two-step acid–base catalyzed transesterification process carried at optimum temperature of both the steps which took about 6 h for complete conversion of TG to ME.

Contents

1. Introduction

The growth of industries, transport, agriculture and other human needs depends largely on petroleum fuels and the per capita energy consumption of a nation is the indication of its economic property. In recent years, the fossil fuel resources are depleting rapidly with consequent environment degradation. Further, India is importing more than 80% of its fuel requirement and spending a huge amount of foreign currency on fuel. Before a serious catastrophic stage arrives, it becomes highly imperative to search alternative fuel options based on renewable energy. Biodiesel is becoming more and more important can prove to be a substitute of diesel and can be produced from vegetable oil resources, particularly, non-edible one oil resources [1]. Biodiesel,

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the monoalkyl esters of long chain fatty acids derived from a renewable lipid feedstocks such as vegetable oil or animal fat, is providing a substitute of or additive to diesel in developing as well as developed countries [2,3]. In India, fuel ethanol and biodiesel are acquiring special importance from energy security and environmental concerns point of view as it can offer large scale employment in the growing and processing of resource particularly in rural areas [4]. The main advantages of biodiesel are its renewability, better quality of exhaust gas emissions, its biodegradability and its contribution to the reduction in CO_2 emissions [5]. The biodiesel can be prepared by transesterification process combining vegetable oils with alcohol in the presence of the catalyst to form fatty acid alkyl esters (i.e., biodiesel) and glycerol [5–22]. Methanol is the most commonly used alcohol for transesterification because of its low cost [3,5].

The transesterification of vegetable oil has been a preferred option for the production of biodiesel due to its low cost and simple method. Refined vegetable oils are the best feedstocks for biodiesel production due to high rate of conversion of pure triglycerides (TG) to FAME in short period of time. The alkali and acid-catalyzed processes have proved to be more practical nowadays. An alkali-catalyzed process can achieve high purity and high yield of biodiesel in a short time (30–60 min), though; it is very sensitive to the purity of the reactants [9–11]. Only well refined vegetable oils with less than 1% (w/w) free fatty acid (FFA) were transesterified by Zhang et al. [12] who compared different processes of biodiesel production and found that alkali-catalyzed process is the simplest one but had a higher raw material cost compared to other processes. For the oils with high FFA contents, either the acid-catalyzed or two-step acid–base catalyzed processes are preferred which requires excess of methanol. In the later case, the first acid-catalyzed step is used to reduce FFA to <1% (w/w) followed by base catalyzed transesterification for the conversion of TG to ME [12–16].

The consumption of edible oil in India is very high and still the indigenous production does not cope with the consumption and hence considerable amount is imported. There is therefore very little chance of using edible oils for biodiesel production to ensure food security aspect. However, the non-edible oil resources can be feedstocks for biodiesel production. There can be grown on waste/semi arid lands under National Biodiesel Programme of Govt. of India and potential availability of non-edible oils in India is about 1 million ton per year. *Madhuca indica*, *Shorea robusta*, *Pongamia glabra*, *Mesua*, *Mallotus Philippines*, *Garcinia indica*, *Jatropha curcas* and *Salvadova* have been identified as non-edible oil resources. Further, with introducing of fast food centres and restaurants in India, lot of waste cooking oil will be available for conversion to biodiesel. Out of the above resources, JCO has been considered for present study.

Commercially available crude oils and fats contain considerable amount of free fatty acids (FFAs) that react with the base catalyst and form saponified products during base catalyzed transesterification which requires exhaustive and costly purification of the products. The saponification not only consumes the alkali catalyst but also causes the formation of emulsions which create difficulties in downstream recovery and purification of the biodiesel. The oil quality has a direct relationship with the technology of transesterification. The oils having high FFA need different processes for biodiesel production than low FFA oils. Therefore chemical analysis with respect to FFA and their consumption is a must. The JCO was purchased in 2007 and its long storage has resulted in the increase of FFA s and so it puts limitation on its base transesterification. Since, the FFA in JCO is more than 2.0% (w/w), it is necessary to reduce FFA (<0.5%) by esterification using acid-catalyst followed by base alkali-catalyzed transesterification [47]. Transesterification of triglycerides with low molecular weight alcohols catalyzed by homogeneous catalysis is the most used one [50–57].

2. Literature review

Numerous studies have been carried out on the kinetics of transesterification processes, biodiesel purification, fuel properties and use in diesel engine. The current challenges are to reduce its production cost which is still higher than petrodiesel due to higher cost of non-edible oil resources.

The kinetics for both acid and base catalyzed transesterification reaction are reported by many authors. Dufek et al. [23] have studied the acid-catalyzed esterification and transesterification of 9-(16)-carboxystearic acid and its mono and di-methyl esters and reported unequal chemical reactivity for different carboxyl and carboxyl methyl groups. Freedman et al. [24] reported the transesterification of soyabean and other oils with methanol and butanol to examine the effect of alcohol type, the reaction rate constants, catalyst type and concentration. Noureddini and Zhu [25] studied the effect of mixing of soyabean oil with methanol on the kinetics of reaction using one-phase transesterification process and found that the mixing had profound effect on the ME yield. Separate acid-catalyzed, alkali-catalyzed, enzyme-catalyzed, or supercritical transesterification of different oils including JCO has been studied by a number of researchers [26–39]. Diasakov et al. [26] investigated the kinetics of uncatalyzed transesterification reaction of soyabean oil. Kusdiana and Saka [27] reported the results of kinetics of transesterification of rapeseed oil using supercritical method and found that conversion rate of rapeseed oil to biodiesel increases dramatically at reaction temperature of 350 °C with a molar ratio of methanol to oil of 42:1.

Donato et al. [49] carried out analysis for acid-catalyzed homogeneous esterification reaction for biodiesel production from palm oil fatty acids using different concentration of H_2SO_4 and other acids as acid catalysts and methanol and ethanol as alcohol and evaluated the optimum concentration in terms of reaction rates, yield of alkyl ester and activation energies. Asakuma et al. [58] have evaluated the activation energies of transesterification of various triglycerides using Gaussion software and found that the effect of structure of TG on the reactivity is not particularly large. Barnwal and Sharma [3] carried out the techno-economic analysis of biodiesel production from different oil feedstocks and found that pongamia, a non-edible oil, can yield biodiesel @ Rs. 10.50/L compared to diesel (Rs. 22/L) at that time and seasam oil gave costliest biodiesel @ Rs. 54/L. The land requirement for growing Jatropha plants for meeting the requirement of different blends of biodiesel with diesel like B_5, B_{10} and B_{20} were calculated for the buses of Uttar Pradesh State Road Transport Corporation (UPSRTC) and reported in our earlier paper [22,35]. Saiffudin and Chau [38] studied the transesterification of used frying oil with 0.5% NaOH in ethanol using microwave irradiation and found that there is considerable enhancement in the reaction rates. Acid-catalyzed production of biodiesel from waste cooking oil was studied by Zhang et al. [12,16] who reported that transesterification is a pseudo first order reaction requiring large excess methanol yielding biodiesel up to 99%. Further, several authors have used the methods involving costly chemicals and requiring much time and efforts for the analysis of intermediate reaction products during the course of kinetics study of transesterification but Kusdiana and Saka [27] have used % yield of methyl ester as the only parameter to monitor the rate of reaction and that three step conversion from TG-DG, DG-MG and MG-ME has been simplified in terms of conversion of TG to ME.

Khan [36] have developed the quantitative analysis of the product mixture formed during transesterification reaction. Mittelbach and co-worker [37] carried out analysis of glycerol after dramatization with N,O-bis(trimethylsilyl) trifluoro acetamida (BSTFA) directly in vegetable oil methyl ester. Capillary GC was used for the analysis of mono, di and triglyceride in methyl

ester. Some authors [28–34] have reported that fuels with higher cetane index gave a lower emission of NOx, HC, CO, HCHO, CH_3CHO, and HCOOH in the exhaust of the engines. In view of the above, it is seen that little work is reported on the Kinetics of two-step transesterification of high FFA oils. Accordingly, the present paper reports the results of simplified Kinetics of transesterification carried out with respect to ME yield only which is not only simple but also less time consuming and less costly compared to separate acid-catalyzed process which takes much longer time for its completion as evidenced by limited reports available in the literature. Ahn et al. [59] followed a two-step reaction process to produce biodiesel. Using this method canola methyl ester (CME), rapeseed methyl ester (RME), linseed methyl ester (LME), beef tallow ester (BTE) and sunflower methyl ester (SME) in a batch reactor using sodium hydroxide, potassium hydroxide and sodium methoxide as catalysts. Cvengro and Povaz [60] described biodiesel production using two-stage low-temperature transesterification of cold pressed rapeseed oil with methanol at temperatures up to 70 °C. Boocock et al. [6–8] have reported that one step base catalyzed methanolysis of soyabean oil using tetrahydrofuran as co-solvent, has been found suitable if oil has FFA less than 1%.

Waste frying oils transesterification was studied by Felizardo et al. [61] to achieve the best conditions for biodiesel production. Miao and Wu [62] introduced an integrated method for the production of biodiesel from microalgal oil. The results suggested that the new process, which combined bioengineering and transesterification, was a feasible and effective method for the production of high quality biodiesel from microalgal oil. Zhu et al. [63] produced biodiesel from *J. curcas* oil using a heterogeneous solid super base catalyst (calcium oxide). Li et al. [64] optimized the whole-cell-catalyzed methanolysis of soybean oil for biodiesel production using response surface methodology. Transesterification reaction of used frying oil by means of ethanol, using sodium hydroxide, potassium hydroxide, sodium methoxide, and potassium methoxide as catalysts, was studied by Encinar et al. [65]. Issariyakul et al. [66] studied the production of biodiesel from waste fryer grease using mixed methanol/ethanol system. Chisti [67] discussed the biodiesel production from microalgae. A packed-bed reactor (PBR) system using fungus whole-cell biocatalyst has developed for biodiesel fuel production by plant oil methanolysis was developed by Hama et al. [68]. Fatty acids methyl esters were prepared by Hernando et al. [69] under microwave irradiation using homogeneous catalysis, either in batch or in a continuous flow system and reported that the process using microwaves irradiation proved to be a faster method for alcoholysis of triglycerides with methanol to get high yields of fatty acid methyl ester [69].

Jain and Sharma [70] has reported a extensive review on the all type of stabilities of biodiesel with respect to time. That will also be helpful while producing biodiesel. Jain and Sharma [71] have evaluated the performance of diesel engine–generator system using biodiesel from WCO and its blends with biodiesel and reported that degradation in efficiency of engine is very less while using B_{20} blend.

Demirbas [72] studied a non-catalytic biodiesel production with supercritical methanol, which allows a simple process and high yield because of the simultaneous transesterification of triglycerides and methyl esterification of fatty acids. Non-catalytic biodiesel production technologies from oils/fats in plants and animals developed by Imahara et al. [73] employing supercritical methanol.

Patil et al. [74] has optimized the biodiesel production from edible and non-edible seeds. The production of fuel quality biodiesel from low-cost high FFA jatropha and karanja oil was investigated. A two-step transesterification process was used to convert the high FFA jatropha and karanja oil to its esters. It was found that the high FFA oils could not be transesterified with the alkali catalyst transesterification process. Yang et al. [75] has studied the feasibility of producing biodiesel from *Idesia polycarpa* var. *vestita* fruit oil and found that fuel properties of the *I. polycarpa* fruit oil biodiesel obtained are similar to the No. 0 light diesel fuel and most of the parameters comply with the limits established by specifications for biodiesel.

3. Material and methods

J. curcas oil was purchased from Jatropha Vikas Sansthaan, New Delhi in the year December 2007. All the chemicals like H_2SO_4, KOH, methanol, anhydrous Na_2SO_4, etc. used were of analytical reagent grade and 99% pure (Naveen Traders).

Raw JCO was filtered to remove all insoluble impurities followed by heating at 100 °C for 10 min to remove all the moisture. The fatty acid compositions of JCO as determined by gas chromatography are shown in Table 1. The fuel properties of refined JCO were determined as per standard methods and are reported in Table 2.

The above table indicates that about 75.3% fatty acids are unsaturated and therefore JCO has high saponification value, i.e., 198.55 mg KOH/g oil which can be computed from the following equation [13].

$$SV = 268 - (0.418 \times P) - (1.30 \times S) - (0.695 \times O) - (0.77 \times L) - (0.847 \times LL)$$

The experiments were conducted in a batch reactor of 1.5 L capacity equipped with condenser, stirrer, inlet and outlet ports and temperature measurement instrument. The whole setup was put in constant temperature water bath (±0.5 °C) as shown in Fig. 1.

The samples were analyzed for ME formation at a predetermined interval of time by Gas Chromatograph (Netal make) equipped with a flame ionization detector and a capillary column for injecting the sample. The GC oven was kept at 230 °C (5 °C/min). Nitrogen was used as carrier gas. Quantitative analysis of %ME was done using European standard EN 14103:2003 [48]. The %ME yield was calculated using Eq. (1). Free fatty acids in the samples were determined using stock solution (Methyl heptadecanoate and n-heptane).

$$\%\text{ of ME} = \frac{\Sigma A - A_{EI}}{A_{EI}} \times \frac{C_{EI} - V_{EI}}{m} \times 100 \quad (1)$$

Table 1
Fatty acid composition of *Jatropha curcas* oil.

Fatty acid	Formula	Systematic Name	Structure	% Amount
Palmitic acid (P)	$C_{16}H_{32}O_2$ $CH_3(CH_2)_{14}COOH$	Hexadecanoic acid	C_{16}	14.1
Palmitolileic acid	$C_{16}H_{30}O_2$ $CH_3(CH_2)_5CH{=}CH{-}(CH_2)_7{-}COOH$	Cis-9 hexadecnoic acid	$C_{16:1}$	0.5
Stearic acid (S)	$C_{18}H_{38}O_2$ $CH_3(CH_2)_{16}COOH$	Octadecanoic acid	C_{18}	6.8
Oleic acid (O)	$C_{18}H_{34}O_2$ $CH_3(CH_2)_7{-}CH{=}CH{-}(CH_2)_7COOH$	Cis9-Octadecanoic acid	$C_{18:1}$	38.6
Linoleic acid (L)	$C_{18}H_{32}O_2$ $CH_3(CH_2)_4$ $CH{=}CH{-}CH_2{-}CH{=}CH{-}(CH_2)_7COOH$	cis-9-cis-12-Octadecadeneoic acid	$C_{18:2}$	36.0
Linolenic acid (LL)	$C_{18}H_{30}O_2$ $CH_3(CH_2)_4CH{=}CH{-}CH_2{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}(CH_2)_4COOH$	cis-6-cis-9-cis-12 Octadecatrienoic acid	$C_{18:3}$	0.2
Arachidice acid	$C_{20}H_{40}O_2CH_3{-}(CH_2)_{18}COOH$	Eicosanoic acid	C_{20}	0.2
Gadolic Acid	$C_{20}H_{36}O_2$		C_{24}	3.6

Table 2
Fuel Properties of *Jatropha curcas* Oil.

S. No.	Properties	*Jatropha curcas* oil
1	Density (kg/m^3 @ 15 °C)	932
2	Viscosity (cSt, @ 30 °C)	51
3	Flash point (°C)	242
4	FFA contents (%)	21.5
5	Gross calorific value (MJ/kg)	37.01

ΣA is total peak area from the methyl ester in C_{14} to that in $C_{24:1}$; A_{EI} is peak area corresponding to methyl heptadecanoate; C_{EI} is concentration of the to methyl heptadecanoate solution (mg/ml); V_{EI} is volume of the to methyl heptadecanoate solution (ml); m is mass of the sample (mg).

4. Experimental procedure

The experiments were performed at different temperatures using different concentrations of H_2SO_4 and NaOH in acid and base catalyzed reactions with respect to ME yield. Due to high FFA contents of *J. curcas* oil (21.5%), a two-step process was selected for converting oil into methyl ester. The acid-catalyzed esterification was used to reduce the FFA to <1% using H_2SO_4 as catalyst at an optimum temperature. The resulting oil having <1% FFA was finally subjected to base catalyzed transesterification at optimum temperature to produce ME. The procedure is described as under:

4.1. Acid pretreatment step

The refined and moisture free oil was poured into the reactor and heated at different temperatures (20, 30, 40, 50, 60, 70 and 80 °C) to optimize the temperature for maximum yield and maximum FFA reduction. The mixture of concentrated H_2SO_4 (0.5%, 1%, 1.5%, 2% and 3%, w/w) with methanol (30%, v/v) was separately heated at same temperatures (20, 30, 40, 50, 60, 70 and 80 °C) and then added to heated oil in the reactor. The mixture was heated at that temperature for 3 h to complete the esterification. The samples were withdrawn at pre-determined time intervals to calculate %ME yield. After acid-catalyzed transesterification step, the mixture was cooled and allowed to settle overnight. This mixture was finally subjected to base catalyzed reaction, where all the residual acid is neutralized and as such, the acid removal is not required in the above step.

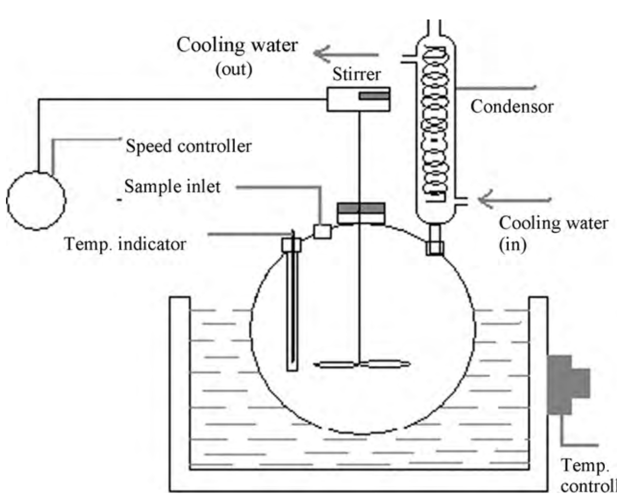


Fig. 1. Schematic diagram of transesterification reactor.

4.2. Base catalyzed transesterification

The esterified oil (<1% FFA) was poured into the reactor and heated at different (20, 30, 40, 50, 60, 70 and 80 °C) to optimize the temperature of reaction for maximum yield. A mixture of NaOH (0.5%, 1%, 1.5%, 2% and 3%, w/w) in methanol was heated at the same temperature (20, 30, 40, 50, 60, 70 and 80 °C) for 5 min and added slowly to the heated oil. The reaction mixture was heated, refluxed and stirred at 400 rpm for about 3 h. The samples were withdrawn at pre-determined time intervals to determine %ME formed. After 3 h, two distinct layers were formed and the mixture was allowed to settle for 2 h or overnight. The heavier glycerol layer was separated from the lighter ME layer by separating funnel.

4.3. Sample treatment

The ME layer was separated, washed with water, heated to remove moisture and dried over anhydrous Na_2SO_4 and checked for its purity using GC, thin layer chromatography and flash point. The rate of reaction was calculated using %ME yield data with respect to time and reaction rate constants and order of reaction was also evaluated along with activation energy of transesterification step and the results are reported in result and discussion part.

5. Results and discussion

The results of variation of ME yield with temperature (20, 30, 40, 50, 60, 70 and 80 °C) using different concentration of H_2SO_4 as acid and NaOH as base catalyst (0.5%, 1%, 1.5%, 2% and 3%, w/w) for esterification and transesterification using optimum amount of methanol i.e. 30% of the oil (v/v) are shown in Fig. 2a and 2b which shows that during esterification, the maximum yield of ME (21.2%) was obtained at 65 °C at 1% (w/w) H_2SO_4 concentration, while during transesterification, 90.1% yield of ME was obtained at 50 °C using 1% NaOH (w/w). The kinetic study of transesterification of JCO has been carried out at the optimum conditions of Temp., catalyst concentration and 400 rpm of stirrer (the later has not

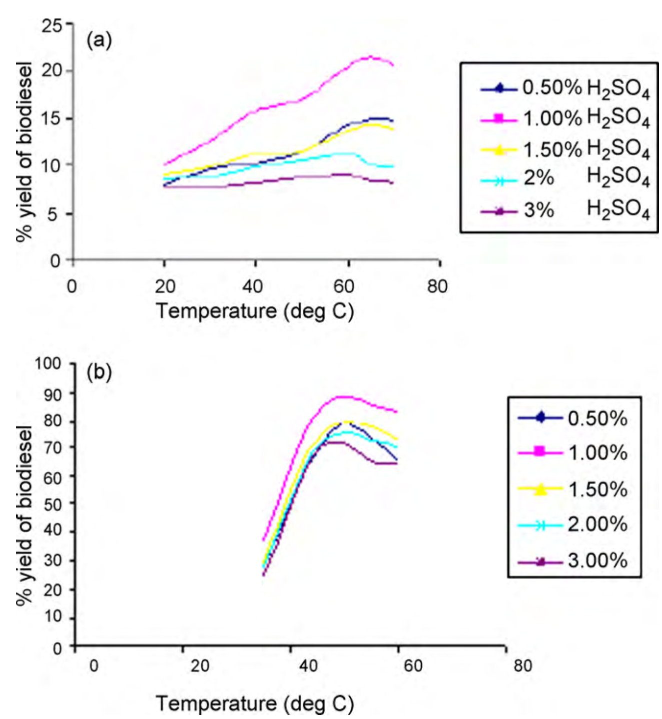


Fig. 2. %ME yield vs temperature (a) acid esterification and (b) base catalyzed transesterification.

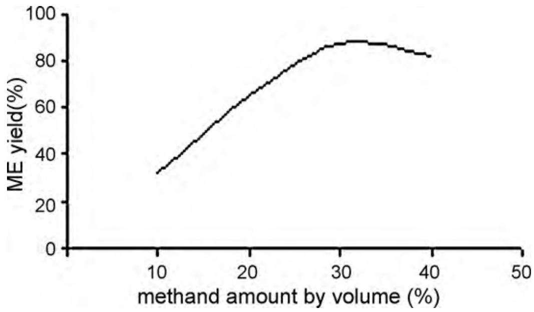


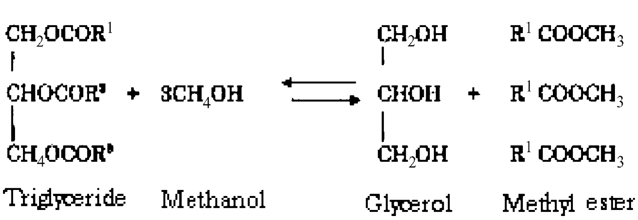
Fig. 3. %ME formed vs % volume of methanol of the oil for transesterification step.

been optimized in the present study). The variation of different amount of methanol as % of oil has been studied with respect to %ME yield under the above optimum conditions and the results are reported in Fig. 3, which shows that a maximum yield of 90.1% of ME was obtained at methanol to oil ratio of 3:7 and therefore this optimum ratio has been used during experimentation. The variation of ME yield with time are shown in Fig. 4a and b which indicates that during esterification, the yield of ME increased with time at a faster rate within first 100 min owing to the faster rate of FFA reduction and thereafter it becomes constant indicating that further conversion of FFA to ME has almost completed within 180 min. Further, the graph of % FFA reduction with time at various methanol to oil ratio (Fig. 5) indicates that 98% conversion of FFA has taken place during 180 min in first step.

While during the base catalyzed transesterification, %ME yield has increased from 21.2% to 90.1% within 180 min. Variation of ME yields vs time (Fig. 4b) shows that no further conversion of TG to ME takes place after this period. The variation of %ME yield vs % FFA reduction as shown in Fig. 6 shows a linear relationship between FFA reduction and ME yield during acid esterification step with a slop of 0.9865 indicating that during acid-catalyzed esterification as the FFA content decreases from 21.5% to less than 1%, ME yield increases up to 21.5% linearly with no further increase in the same.

5.1. Kinetics of transesterification of *Jatropha curcas* oil

Diasakov et al. [26] has reported that the transesterification reaction to proceed in three steps in which TG reacts with methanol to produce diglycerides, which further reacts with methanol to yield monoglycerides that finally reacts with methanol to produce methyl ester and glycerol. Since one mole of methyl ester is generated per mole of methanol reacted at each step, in all, six rate constants are reported in the literature for the whole reaction from TG to methyl ester (biodiesel) as shown by the equation given below:



(2)

According to the above equation, whole transesterification results ultimately in the production of methyl ester and therefore, all the intermediate reaction products (e.g. DG and MG) can be ignored and simple mathematical model expressing the whole conversion as one step has been developed. The whole reaction is considered to proceed as first order reaction as a function of ME yield [26]. Accordingly, the kinetics of transesterification has been studied with respect to %ME yield as a function of time. The rates of reaction were determined using the above data.

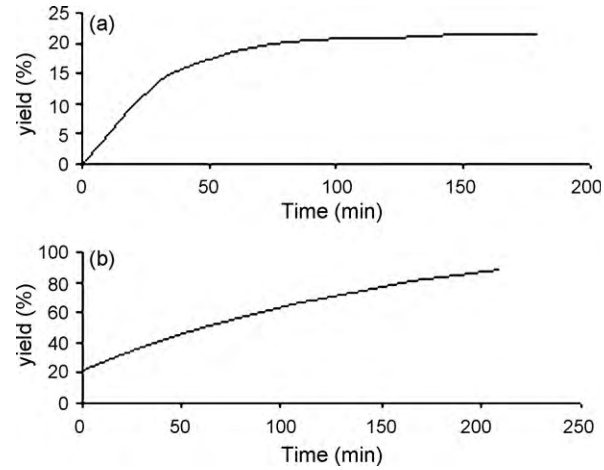


Fig. 4. %ME Yield vs time (a) acid esterification and (b) base transesterification.

The reaction rate constant can be expressed by:

$$\text{rate} = \frac{d(\text{ME})}{dt} \tag{2}$$

where () represents the %ME yield.

It can be modified as

$$\frac{d(\text{ME})}{dt} = k(\text{ME})$$

where (ME) refers to the %ME yield. Assuming that the initial concentration of ME at time $t = 0$ is ME_0 and that it increases to ME_t at time t. The integration of this equation gives:

$$\int_{\text{ME}_0}^{\text{ME}_t} \frac{d(\text{ME})}{(\text{ME})} = k\int_0^t dt$$

and

$$\ln\frac{(\text{ME}_t)}{\text{ME}_0} = kt$$

or

$$K = \frac{\ln(\text{ME}_t) - \ln(\text{ME}_0)}{t} \tag{3}$$

Using ME yield data obtained at different times, the reaction rate constants of 0.0031 and 0.008 min^{-1} were calculated for esterification and transesterification reaction, respectively. This indicates that the rate of reaction of acid-catalyzed esterification is slower than base catalyzed transesterification perhaps due to the presence of considerable amount of intermediate reaction products interfering in the transformation to methyl ester [40]. This observation is in contrast to the faster rate of esterification

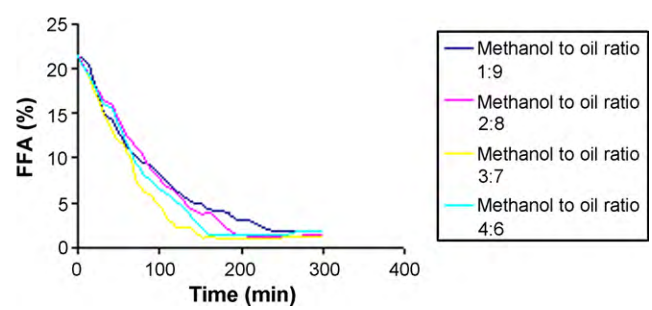


Fig. 5. Variation of FFA vs time for different methanol to oil ratio (v/v) during acid-catalyzed step.

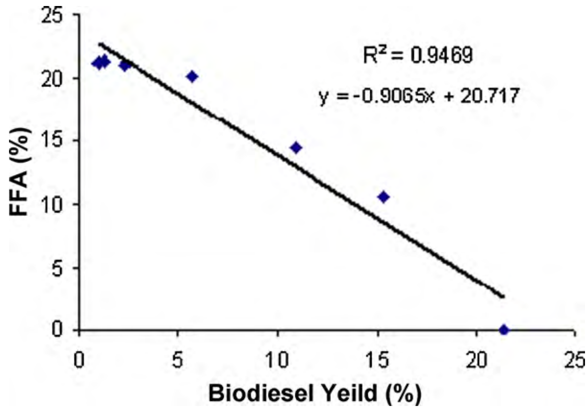


Fig. 6. Variation of %ME yield (%) with % to FFA reduction during acid transesterification.

reaction compared to slow transesterification under supercritical transesterification conditions [41]. Due to this reason the conversion of high FFA oil take longer time to convert to ME compared to oil with low FFA. Further, a plot of dME/dt vs yield using log graph gives straight line for both esterification and transesterification reaction as shown in Fig. 7a and b which indicates that both the reaction are of first order. This also indicates that the rate of reaction varies linearly with yield. The slop of straight line for esterification and transesterification respectively are given by Eqs. (4) and (5) which indicates that rates of reaction varies linearly with yield.

For acid transesterification:

$$\ln\left(\frac{\mathrm{dME}}{\mathrm{d}t}\right) = -0.0883\ln(\mathrm{ME}) + 2.67 \quad (R^2 = 0.918) \tag{4}$$

For base transesterification:

$$\ln\left(\frac{\mathrm{dME}}{\mathrm{d}t}\right) = -1.0714\ln(\mathrm{ME}) + 2.868 \quad (R^2 = 0.947) \tag{5}$$

The slop of the straight line in Fig. 7a and b was found as −0.0883 and −1.0714 with a value of R^2 of 0.918 and 0.947 indicating that the data collected are 91.8% accurate for esterification and 94.7% accurate for transesterification reaction.

Using Eq. (3), the reaction rate constant under optimum conditions of temperature, catalyst concentration, methanol and rpm of stirring, has been computed as 0.0031 and 0.008 min^{-1} for esterification and transesterification respectively indicating that the former reaction is slower than the later and are in close proximity with the results reported by Schuchardt et al. [42] who found that transesterification reaction catalyzed by Brownsted acids, sulphonic acid and sulphuric acids are slower and take more than 3 h to complete the conversion but give relatively higher yields of ME. Further, the transesterification was carried out at various temperature for different time and ME yield was calculated and the results as shown in Fig. 8 indicates that maximum yield of ME (90.1%) occurred at 50 °C compare to other temperatures. Above 50 °C, there is very little increase in ME yield [42].

The results of variation of %ME yield with times at various temperatures as given in Fig. 8 indicates that during base catalyzed transesterification, the maximum yield of 90.1% ME was obtained in 180 min when reaction temperature was 50 °C. A plot of k vs temperature as shown in Fig. 9 shows that the rate of reaction increases linearly with increase in the reaction temperature with a slop 0.0004 and follows the first order reaction which is in agreement with literature [24,43,49,55]. The figure also indicates that the rates of reaction beyond 50 °C also increases with increase in temperature but the ME yield decreases considerably (Fig. 2b).

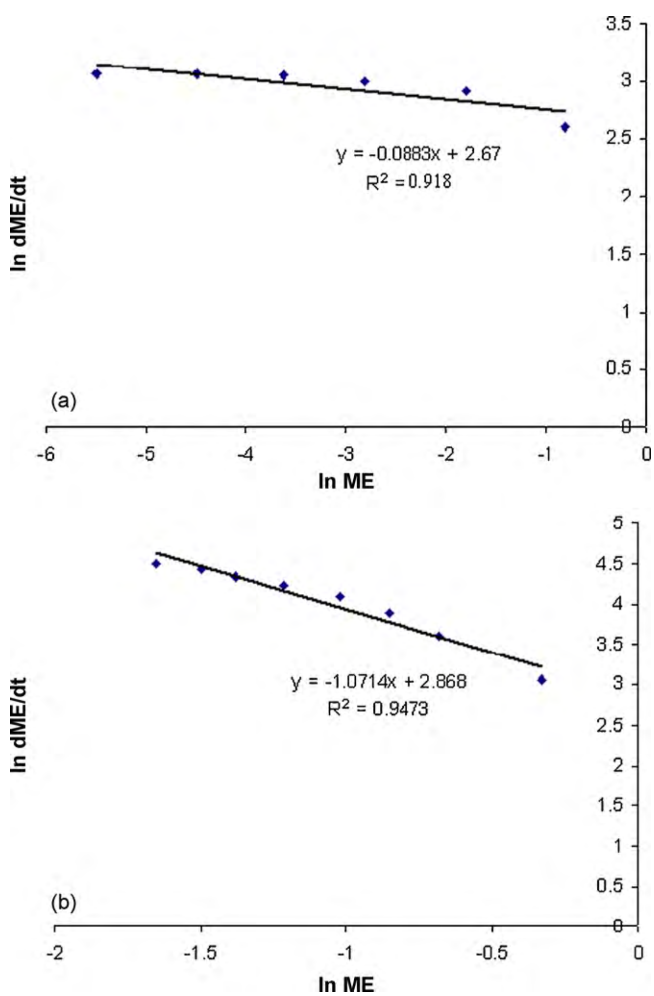


Fig. 7. Plot of reaction rate vs yield on logarithmic graph (%) for esterification and base transesterification of JCO.

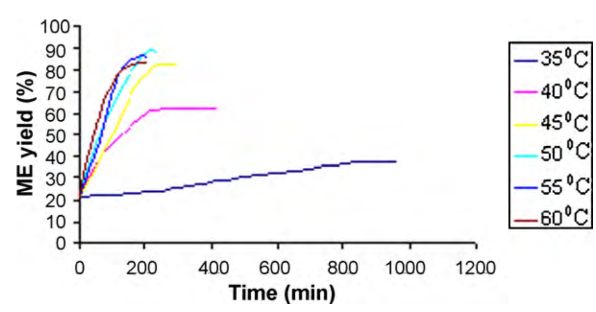


Fig. 8. ME yield vs time for various temperatures.

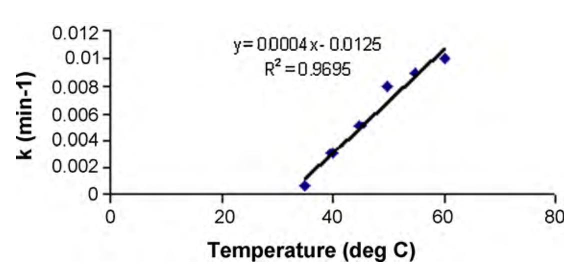


Fig. 9. Variation of rate reaction constant with temperature.

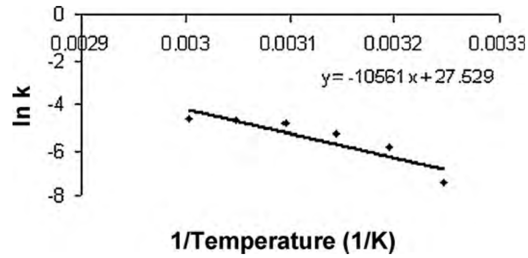


Fig. 10. Plot of ln k vs $1/T$.

Table 3
Optimum conditions for biodiesel production.

Parameters	Esterification	Transesterification
Methanol to oil ratio (v/v)	3:7	3:7
Catalyst concentration (w/w)	1% H_2SO_4	1% NaOH
Temperature (°C)	65 ± 0.5	50 ± 0.5
RPM	400	400
Time (min)	180	180
Yield (%)	21.2	90.1
Reaction rate constant (min^{-1})	0.0031	0.008

The quantitative relationship between the activation energy (E_a) and reaction rate at given time is given by Arrhenius Eq. (6):

$$E_a = -RT\ln\left(\frac{k}{A}\right) \tag{6}$$

where A is the frequency factor for the reaction, R the universal molar gas constant, and T the temperature (K). Since the activation energy is dependent on temperature, and therefore the rate constants at any temperature (within the validity of the Arrhenius equation) [56] can be computed using Eq. (7):

$$\ln k = \ln A - \frac{E_a}{RT} \tag{7}$$

Eq. (7) is a linear equation and therefore a plot of ln k and $1/T$ is given in Fig. 10 also validates the reaction order. Activation energy (E_a) has been calculated using Fig. 10 which is 87808.37 J/mol.

A number of investigators studied the kinetics of supercritical transesterification at various temperatures and pressures and reported that reaction rate constants increase with increase in temperature [43] while the present study was carried out at an optimum temperature of 65° and 50 °C for esterification and transesterification respectively under optimum conditions of acid and base concentration, methanol to oil ratio, temperature, rpm, etc. under atmospheric pressure conditions. All the optimized parameters for biodiesel production are given in Table 3. This is first study of simple transesterification kinetics carried out at pre-determined temperature and atmospheric pressure. The rate of esterification as well as transesterification were studied with respect to %ME yield. It is not only simple but also less costlier and less time consuming compared to that involves the estimation of six different rate constants involving complex reactions from TG–MG, DG–MG and MG–ME at different temperatures and pressures as reported by Fukuda et al. [44], Merchetti et al. [45] and Karnee et al. [46]. The simple acid–base transesterification of JCO for biodiesel production has also been reported for the first time contrary to the work on separate acid or base or enzyme catalyzed processes.

6. Conclusions

The present study deals with the kinetics of two-step acid–base catalyzed transesterification of high FFA containing *J. curcas* oil under optimum conditions of methanol to oil ratio of 3:10 (v/v), temperature of 65 and 50 °C for acid and base transesterification, respectively, 400 rpm and catalyst concentration of 1% (w/w) for H_2SO_4 and 1% (w/w) for NaOH. The kinetics has been studied with respect to ME yield directly from TG by ignoring the complex reactions determining six different reaction rate constants which is not only time consuming but costlier and needs much efforts. The rate constant of both the reaction are found as 0.0031 and 0.008 min^{-1}, respectively, indicating that the former is slower than the later reaction. The yield of ME from esterification and transesterification are found as 21.2% and 90.1%, respectively. This also represents that the energy required for the transesterification to occur is also very small which is calculated as 87808.37 J/mol. Such low energy process can be very useful for 'on farm' biodiesel production from high FFA oils and offers opportunities for energizing remote areas through rural electrification. The process can find wide application for the conversion of high FFA oils, especially, non-edible oils which may have more FFA during long term storage of the resource due to their poor oxidation stabilities.

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